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Physico-chemical Studies of Ternary Chelates in Solution: Part I—Potentiometric Study of Ni(II)-Glycine-Phenylacetohydroxamic Acid System

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Formation of ternary chelates in solution involving simultaneous chelation of two ligands has been studied. Stability constant of Ni^{2+}-glycine-phenylacetohydroxamic acid system has been determined potentiometrically at 30° and $\mu = 0{\cdot}1$. All possible equilibria involving protonated and unprotonated ternary chelates have been considered and their equilibrium constants calculated by setting up suitable simultaneous equations and solving them using the data obtained from the *p*H-titration curves. A very simple method of arriving at the overall stability constants of unprotonated ternary chelates is also described.

FORMATION of ternary chelates in solution have been reported by many workers[1]. Most of the work is on the systems involving ligands which combine in different *p*H-regions[2-5]. Only a few references are available concerning ternary chelates in which two ligands combine with a metal ion in overlapping *p*H regions[6-8]. As glycine (Gly) and 2-phenylacetohydroxamic acid (PAHA) were found to combine with Ni^{2+} in overlapping *p*H regions, we have undertaken a detailed potentiometric study of the ternary system Ni^{2+}-Gly-PAHA. A simple method of calculating the overall stability constants and an elaborate method of evaluating the equilibrium constants of various equilibria involving possible protonated and unprotonated species that could exist in the ternary system are described in the present study.

Materials and Methods

PAHA was prepared by the action of hydroxylamine on methyl phenylacetate[9]. Glycine (Riedel) was used as such. Nickel perchlorate was prepared and estimated by conventional methods. The experiments were carried out using a Leeds and Northrup *p*H meter fitted with glass and calomel electrodes.

The procedure consisted of the titration of PAHA ($10^{-3}M$), glycine ($10^{-3}M$), 1:1 and 1:2 mixtures of Ni^{2+} and PAHA or glycine ($10^{-3}M$) and 1:1:1 mixture of Ni^{2+}, PAHA and glycine ($10^{-3}M$) against CO_2 free sodium hydroxide ($10^{-1}M$). All the above solutions were acidified with $2\times10^{-3}M$ perchloric acid and the ionic strength was maintained constant (0·1) by adding sodium perchlorate.

Calculation of stability constants — Two methods were employed to calculate the stability constants of the ternary chelate. In the first method formation of only unprotonated ternary chelate was considered. In the other method all the species that could exist under experimental conditions were considered.

Method-1 — This method which in principle could be considered as an extension of the Irving-Rossotti method assumes formation of the ternary chelate in a single step. To simplify the calculations a composite curve[10] was constructed out of the PAHA and glycine *p*H titration curves. From the horizontal distances between this composite curve and the curve of the ternary system, $\bar{n}$ and pL values were calculated using the expressions given by Irving and Rossotti[11]. Then the overall stability constant was taken as $\log K^{M}_{MAB} = pL_{0\cdot5} + pL_{1\cdot5}$. In other words this treatment considers the two ligands PAHA and glycine as a single group, whose pK_a value could be calculated from the composite curve. Now the addition of one equivalent each of PAHA and glycine was considered as the addition of two equivalents of this composite group and hence, the formation equilibrium could be represented as

$$Ni^{2+} + 2(HA.HB) \rightleftharpoons NiAB + 2H^{+} \quad \ldots(1)$$

where HA and HB represent PAHA and glycine respectively. Thus by considering a hypothetical composite group, the ternary system could be treated as a binary one.

Method-2 — In this method all the possible protonated and unprotonated species such as HA, A, HB, B, NiA, NiHA, NiA_2, $NiHA_2$, NiH_2A_2, NiB, NiHB NiB_2, NiHB, NiH_2B_2 NiAB, NiHAB and NiH_2AB (charges being omitted here and elsewhere for the sake of clarity), that could exist under experimental conditions used were considered. In order to simplify the calculations, the formation constants of all the binary protonated and unprotonated species were determined separately.

Formation constants of protonated and unprotonated 1:1 *complexes* — Using the data from the *p*H titration curves of ligand and metal ion in 1:1 ratio the formation constants of protonated and unprotonated 1:1 complexes were calculated. As a first approximation formation of 1:2 complexes were neglected and thus the expressions for total ligand (T_A) and total metal (T_M) could be written as

$$T_A = [HA] + [A] + [MA] + [MHA] \quad \ldots(2)$$

$$T_M = [M] + [MA] + [MHA] \quad \ldots(3)$$

From the horizontal distances of *p*H titration curves of ligand in the presence and absence of metal ion $\bar{n}$ values were calculated. The expressions (4) and (5) were used for calculating the [A] and [M] of this system.

$$[A] = \frac{(1-\bar{n})T_L}{1+[H]/K_A} \quad ...(4)$$

$$[M] = [A](1+[H]/K_A) \quad ...(5)$$

These values obtained at two different $\bar{n}$ values were substituted in the Eq. (6)

$$[M][A]K^M_{MA} + \frac{[M][A][H]}{K_A}K^M_{MHA} = \bar{n}T_M \quad ...(6)$$

and the two simultaneous equations thus obtained were then solved for K^M_{MA} and K^M_{MHA}. These operations were repeated by taking various pairs of $\bar{n}$ values from which average K^M_{MA} and K^M_{MHA} values were computed. The values of K^M_{MB} and K^M_{MHB} were also similarly computed.

Formation constants of protonated and unprotonated 1:2 *complexes* — The formation constants of protonated and unprotonated 1:2 complexes were calculated using the data from *p*H titration curves obtained from the titration of metal and ligand in 1:2 ratio. Considering the existence of species A, HA, MA, MHA, MA_2, MHA_2 and MH_2A_2, the expressions for T_M and T_A come out to be

$$T_A = [A]+[HA]+[MA]+[MHA]+2[MHA_2]+2[MA_2]+2[MH_2A_2] \quad ...(7)$$

$$T_M = [M]+[MA]+[MHA]+[MHA_2]+[MH_2A_2]+[MA_2] \quad ...(8)$$

Using $\bar{n}$ values calculated from the experimental titration curves, [A] and [M] were calculated from the expressions (9) and (10)

$$[A] = \frac{T_A-\bar{n}T_M}{1+[H]/K_A} \quad ...(9)$$

$$[M] = \frac{X_A}{2+K^M_{MA}[A]+K^M_{MHA}\frac{[H][A]}{K_A}} \quad ...(10)$$

where

$$X_A = [A](1+[H]/K_A)$$

In the above calculations previously determined value of K^M_{MA} and K^M_{MHA} were used. Three simultaneous equations were obtained by substituting [M] and [A] values at three $\bar{n}$ values in Eq. (11).

$$[M][A]^2K^M_{MA}\left(K^{MA}_{MA_2}+[H]K^{MHA}_{MA_2H}K^{MA}_{MHA}+\frac{K^{MAH}_{MA_2H_2}K^{MA}_{MAH}}{K_A}\right) = [M]+T_A-T_M-X_A \quad ...(11)$$

A 3×3 determinant was constructed using the three simultaneous equations and by applying Crammers rule this determinant was solved for $K^{MA}_{MA_2}$ $K^{MAH}_{MA_2H}$ and $K^{MAH}_{MA_2H_2}$. Different sets of $\bar{n}$ values were used to calculate the average values of these equilibrium constants.

Now the approximation that 1:2 complexes do not exist during the 1:1 titration could be removed and a better set of values obtained by calculating K^M_{MHA} and K^M_{MA} using the data from the 1:1 titration curve with the help of Eqs. (12-14)

$$[A] = \frac{T_A-\bar{n}T_M}{1+[H]/K_A} \quad ...(12)$$

$$[M] = X_A/P \quad ...(13)$$

$$\text{and } K^M_{MA}[M][A]+K^M_{MHA}\frac{[M][A][H]}{K_A} = T_M-[M]P \quad ...(14)$$

where

$$P = 1+K^M_{MA_2}[A]^2+K^{MA_2}_{MHA_2}K^M_{MA_2}[A]^2[H](1+K^{MHA_2}_{MH_2A_2}[H])$$

These modified values were used to get more accurate values of $K^{MA}_{MA_2}$, $K^{MAH}_{MA_2H}$ and $K^{MAH}_{MA_2H_2}$ from the data of 1:2 titration curve. This process of refining was continued till the values obtained from two successive operations were essentially same.

Formation constants of protonated and unprotonated 1:1:1 *complexes* — The data from the titration curve with metal ion, HA and HB in 1:1:1 ratio was used to calculate the formation constants of protonated and unprotonated 1:1:1 complexes. In addition to the species considered for the 1:1 and 1:2 titrations MAB, MHAB and MH_2AB were also considered. Now the expressions for T_L and T_M could be written as:

$$T_L = [A]+[B]+[HA]+[HB]+[MA]+[MHA]+[MB]+[MHB]+2[MA_2]+2[MHA_2]+2[MH_2A_2]+2[MB_2]+2[MHB_2]+2[MH_2B_2]+2[MAB]+2[MHAB]+2[MH_2AB] \quad ...(15)$$

$$T_M = [M]+[MA]+[MB]+[MA_2]+[MHA]+[MHA_2]+[MH_2A_2]+[MB_2]+[MHB_2]+[MH_2B_2]+[MAB]+[MHAB]+[MH_2AB]+[MHB] \quad ...(16)$$

In order to evaluate the [M], [A] and [B] Eqs. (17-19) were set up

$$X_A+X_B = T_L-\bar{n}T_M \quad ...(17)$$

$$X_A+[M]R_A+[M][A]^2K^M_{MA_2}Z_A = X_B+[M]R_B+[M][B]^2K^M_{MB_2}Z_B \quad ...(18)$$

$$[M] = \frac{X_A+X_B}{2+R_A+R_B} \quad ...(19)$$

where

$$R_A = K^M_{MA}[A]+K^M_{MHA}\frac{[A][H]}{K_A}$$

$$R_B = K^M_{MB}[B]+K^M_{MHB}\frac{[B][H]}{K_B}$$

$$Z_A = 1+K^{MA_2}_{MHA_2}[H]+K^{MA_2}_{MH_2A_2}[H]^2$$

$$Z_B = 1+K^{MB_2}_{MHB_2}[H]+K^{MB_2}_{MH_2B_2}[H]^2$$

As a first approximation $\bar{n}$ value was calculated using the composite curve and the 1:1:1 *p*H titration curve as described in method-1. The known formation constant values of protonated and unprotonated binary chelates were substituted in Eqs. (17), (18) and (19). The resulting simultaneous equations were solved for [M], [A] and [B] at three different points on the *p*H titration curve and substituted in Eq. (20).

$$X_A+X_B+K^M_{MA_2}[M][A]^2R_A+K^M_{MB_2}[M][B]^2R_B+([M][A]\times[B]\left(K^M_{MAB}+K^{MA}_{MHAB}K^M_{MA}\frac{[H]}{K_A}+K^{MHA}_{MH_2AB}K^{MA}_{MHA}K^M_{MA}\frac{[H]^2}{K_B}\right) = T_L-T_M \quad ...(20)$$

The resulting three simultaneous equations were used to construct a 3×3 determinant, which was then solved for K^{M}_{MAB}, K^{MA}_{MHAB} and $K^{MHA}_{MH_2AB}$ by applying Crammer's rule. These operations were repeated using different sets of $\bar{n}$ values and the average K^{M}_{MAB} K^{MA}_{MHAB} and $K^{MHA}_{MH_2AB}$ were computed.

To remove the approximation involved in the calculation of $\bar{n}$ values the approximate values of [M], [A], [B], K^{M}_{MAB} K^{MA}_{MHAB} and $K^{MHA}_{MH_2AB}$ were substituted in Eq. (21)

$$[M][A]\left(K^{M}_{MA}+K^{M}_{MHA}\frac{[H]}{K_A}\right)+[M][B]\left(K^{M}_{MB}+K^{M}_{MHB}\frac{[H]}{K_B}\right)+2K^{M}_{MA_2}[M][A]^2R_A+2K^{M}_{MB_2}[M][B]^2R_B+2[M][A][B]\times\left(K^{M}_{MAB}+K^{MA}_{MHAB}K^{M}_{MA}\frac{[H]}{K_A}+K^{MHA}_{MH_2AB}K^{MA}_{MHA}K^{M}_{MA}\frac{[H]^2}{K_B}\right)=\bar{n}T_M \quad \ldots(21)$$

to get a more consistent value of $\bar{n}$. This $\bar{n}$ value was then used to calculate a better set of [M], [A], [B], K^{M}_{MAB}, K^{MA}_{MHAB} and $K^{MHA}_{MH_2AB}$ values by repeating the above procedure. This process of iteration was continued till the values obtained by two successive operations were constant within the limits of experimental error. All other equilibrium constant values were evaluated by utilizing the simple algebraic relationships that exist between them and the above determined values. All the log K values were found to vary within the limits of $\pm0{\cdot}03$.

Results and Discussion

Fig. 1 reveals that curves IV and V diverge from curves II and III after the addition of 2 ml of NaOH indicating the formation of complexes in solution. That this divergency is continued even after the addition of 3 ml of NaOH could be due to the precipitation of metal hydroxides. Curve VI was found to diverge from all other curves after the addition of 2 ml of NaOH and the divergence continued till metal hydroxides were precipitated after the addition of 4 ml of NaOH. The 1:1:1 experimental curve VI was found to lie far below the theoretical composite curve constructed out of the two 1:1 curves (of MA and MB) revealing that in addition to MA+MHA, MA_2, MHA_2, MH_2, A_2MB+MHB, MB_2, MHB_2 and MH_2B_2 some other new species possibly ternary chelates exist in this system. The following experimental observations further substantiate the ternary chelate formation.

(i) Addition of HA or HB to the 1:1 solution of Ni^{2+} and HB or HA prior to or after the addition of one mole of base per mole of HB or HA decreased the *p*H of the solution.

(ii) *p*H of the solution containing metal ion, HA and HB in 1:1:1 ratio is lower than the *p*H of the solution containing metal ion and HA or HB in 1:2 ratio.

(iii) In the ternary system hydrolysis was found to occur at higher *p*H when compared to that in the binary systems.

(iv) Absorption spectra of the solutions containing M^{2+}, HA and HB in 1:1:1 ratio were significantly different from the spectrum of either of the solutions containing M^{2+} and HA or HB in 1:1 ratio.

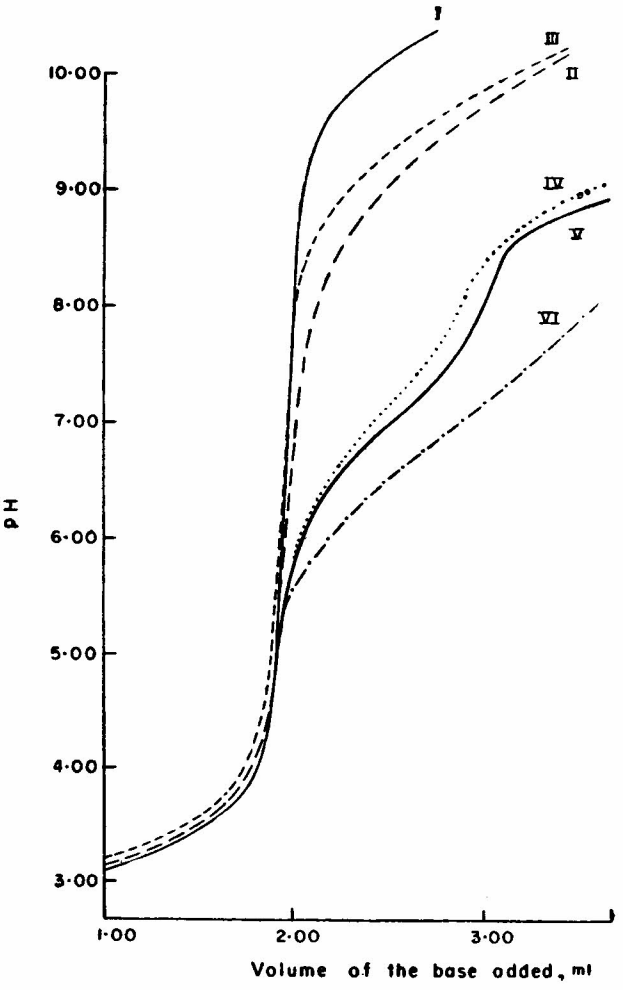


Fig. 1 — *p*H titration curves of Ni^{2+}-PAHA-Gly system [I, perchloric acid ($2\times10^{-3}M$); II, perchloric acid ($2\times10^{-3}M$) +PAHA ($10^{-3}M$); III, perchloric acid ($2\times10^{-3}M$)+glycine ($10^{-3}M$); IV, perchloric acid ($2\times10^{-3}M$)+PAHA ($10^{-3}M$) +Ni^{2+} ($10^{-3}M$); V, perchloric acid ($2\times10^{-3}M$)+glycine ($10^{-3}M$)+ Ni^{2+} ($10^{-3}M$); VI, perchloric acid ($2\times10^{-3}M$) +PAHA ($10^{-3}M$)+glycine ($10^{-3}M$)+Ni^{2+} ($10^{-3}M$)]

Curve VI coincides with curves IV and V at low *p*H regions but as $\bar{n}$ increases beyond 0·20 it gets separated, indicating that both the ligands combine simultaneously with the metal ion.

Of the two methods used for calculating the equilibrium constants, the second method is an exhaustive one but is definitely more cumbersome than the first. The log K^{M}_{MAB} values obtained by method-1 and method-2 were 10·40 and 10·20 respectively. Though the error in log K^{M}_{MAB} value obtained from method-1 is significant it is by no means very large. Hence, it could be inferred that if it is not neccessary to know the nature of the protonated species and very precise log K values are required, method-1 could be used to compute the overall stability constants.

Data in Tables 1 and 2 indicate that $K^{M}_{MB} > K^{M}_{MA}$ and $K^{MB}_{MBA} > K^{MA}_{MAB}$ which is in accordance with the basicities of glycine and PAHA. That log K^{M}_{MB}— log $K^{M}_{MA} > pK_B - pK_A$ indicates that glycine forms

TABLE 1 — EQUILIBRIUM CONSTANTS OF THE BINARY CHELATES

(HA = PAHA; HB = glycine, M = Ni^{2+}, temp. = 30°; $\mu = 0{\cdot}1M$)

Sl No.	Equilibrium	log K	Sl No.	Equilibrium	log K
1	$HA \rightleftharpoons H+A$	−9·25	17	$HB \rightleftharpoons H+B$	−9·60
2	$M+A \rightleftharpoons MA$	5·20	18	$M+B \rightleftharpoons MB$	5·69
3	$M+HA \rightleftharpoons MHA$	1·13	19	$M+HB \rightleftharpoons MHB$	1·75
4	$MA+H \rightleftharpoons MHA$	5·18	20	$MB+H \rightleftharpoons MHB$	5·66
5	$M+HA \rightleftharpoons MA+H$	−4·05	21	$M+HB \rightleftharpoons MBH$	−3·91
6	$M+2A \rightleftharpoons MA_2$	9·16	22	$M+2B \rightleftharpoons MB_2$	10·09
7	$MA+A \rightleftharpoons MA_2$	3·97	23	$MB+B \rightleftharpoons MB_2$	4·40
8	$MA+HA \rightleftharpoons MA_2+H$	−5·29	24	$MB+HB \rightleftharpoons MB_2+H$	−5·19
9	$MA+HA \rightleftharpoons MHA_2$	1·41	25	$MB+HB \rightleftharpoons MHB_2$	2·04
10	$MHA+A \rightleftharpoons MHA_2$	5·48	26	$MHB+B \rightleftharpoons MHB_2$	5·98
11	$MA_2+H \rightleftharpoons MHA_2$	6·69	27	$MB_2+B \rightleftharpoons MHB_2$	7·24
12	$MHA+HA \rightleftharpoons MH_2A_2$	2·67	28	$MHB+HB \rightleftharpoons MH_2B_2$	3·09
13	$MHA+HA \rightleftharpoons MA_2 2H$	−10·47	29	$MHB+HB \rightleftharpoons MB_2+2H$	−10·86
14	$MHA+HA \rightleftharpoons MHA_2+H$	−3·77	30	$MHB+HB \rightleftharpoons MHB_2+H$	−3·65
15	$MHA_2+H \rightleftharpoons MH_2A_2$	6·44	31	$MHB_2+H \rightleftharpoons MH_2B_2$	6·71
16	$MA_2+2H \rightleftharpoons MH_2A_2$	13·44	32	$MB_2+2H \rightleftharpoons MH_2B_2$	13·95

TABLE 2 — EQUILIBRIUM CONSTANTS OF THE TERNARY CHELATES

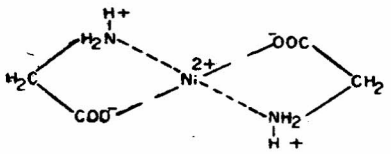
(HA = PAHA; HB = glycine; M = Ni^{2+}; temp. = 30°; $\mu = 0{\cdot}1$)

Sl No.	Equilibrium	log K	Sl No.	Equilibrium	log K
1	$MA+B \rightleftharpoons MAB$	5·00	24	$MHB+HA \rightleftharpoons MHAB+H$	−2·41
2	$MB+A \rightleftharpoons MAB$	4·52	25	$MA_2+MB_2 \rightleftharpoons 2MAB$	1·15
3	$M+A+B \rightleftharpoons MAB$	10·20	26	$MHA_2+MHB_2 \rightleftharpoons 2MHAB$	3·18
4	$MA+HB \rightleftharpoons MHAB$	3·39	27	$MH_2A_2+MH_2B_2 \rightleftharpoons 2MH_2AB$	5·60
5	$MB+HA \rightleftharpoons MHAB$	3·25	28	$MA+MB \rightleftharpoons MAB+M$	−0·69
6	$MHA+B \rightleftharpoons MHAB$	7·81	29	$MA_2+MB \rightleftharpoons MAB+MA$	0·73
7	$MHB+A \rightleftharpoons MHAB$	6·84	30	$MB_2+MA \rightleftharpoons MAB+MB$	0·60
8	$MAB+H \rightleftharpoons MHAB$	7·99	31	$MHA+MB \rightleftharpoons MHAB+M$	2·12
9	$MHA_2+HB \rightleftharpoons MHAB+HA$	1·98	32	$MHB+MA \rightleftharpoons MHAB+M$	1·64
10	$MHA_2+B \rightleftharpoons MHAB+A$	2·33	33	$MHA+MHB \rightleftharpoons MH_2AB+M$	4·24
11	$MHB_2+HA \rightleftharpoons MHAB+HB$	1·21	34	$MHA_2+MHB \rightleftharpoons NH_2AB+MA$	3·96
12	$MHB_2+A \rightleftharpoons MHAB+B$	0·86	35	$MHB_2+MHA \rightleftharpoons MH_2AB+MB$	3·95
13	$MA_2+HB \rightleftharpoons MAB+HA$	0·69	36	$MH_2A_2+MB \rightleftharpoons MH_2AB+MA$	2·48
14	$MA_2+B \rightleftharpoons MAB+A$	1·04	37	$MH_2B_2+MA \rightleftharpoons MH_2AB+MB$	3·12
15	$MB_2+HA \rightleftharpoons MAB+HB$	0·46	38	$MH_2A_2+MB_2 \rightleftharpoons MH_2AB+MAB$	3·78
16	$MB_2+A \rightleftharpoons MAB+B$	0·11	39	$MH_2B_2+MA_2 \rightleftharpoons MH_2AB+MAB$	2·97
17	$MHAB+H \rightleftharpoons MH_2AB$	7·79	40	$MHA_2+MB_2 \rightleftharpoons MHAB+MAB$	2·44
18	$MHA+HB \rightleftharpoons MH_2AB$	5·99	41	$MHB_2+MA_2 \rightleftharpoons MHAB+MAB$	2·89
19	$MHB+HA \rightleftharpoons MH_2AB$	5·37	42	$MH_2A_2+MHB \rightleftharpoons MH_2AB+MHA$	2·70
20	$MAB+2H \rightleftharpoons MH_2AB$	15·77	43	$MH_2B_2+MHA \rightleftharpoons MH_2AB+MHB$	2·90
21	$MHA_2+AB \rightleftharpoons MH_2AB+A$	0·52	44	$MH_2A_2+MHB_2 \rightleftharpoons MH_2AB+MHAB$	4·53
22	$MHB_2+HA \rightleftharpoons MH_2AB+B$	−0·61	45	$MH_2B_2+MHA_2 \rightleftharpoons MH_2AB+MHAB$	4·25
23	$MHA+HB \rightleftharpoons MHAB+H$	−1·80			

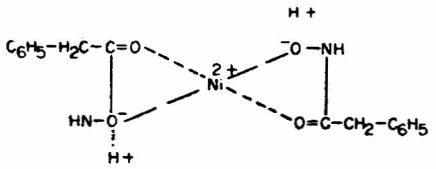
more stable and/or PAHA forms less stable complexes with Ni^{2+} than those expected from their basicities. This could be understood by considering that glycine with one nitrogen and one oxygen as donor atoms induces larger ligand field stabilization[12] as compared to that of PAHA with two oxygen donor atoms when the metal ion is ligand field sensitive Ni^{2+}.

From the data in Table 1 it could be seen that $K^{MA_2}_{MHA_2} > K^{MA}_{MHA}$, $K^{MB_2}_{MHB_2} > K^{MB}_{MHB_2}$, $K^{MHA_2}_{MH_2A_2} > K^{MA}_{MHA}$ and $K^{MHB_2}_{MH_2B_2} > K^{MB}_{MHB}$ indicating the greater protonation tendency of 1:2 and monoprotonated 1 : 2 complexes when compared to the corresponding 1:1 complexes. To understand these observed trends the "polar solvent" model[1,13] could be of some use. According to this model the more polar species would be solvated to a greater extent and hence would be more stable in a polar solvent. Thus the data indicate that in aqueous medium monoprotonated and biprotonated 1:2 complexes are more polar than the monoprotonated 1:1 complex. The log K values of equilibria (10) and (11) (Table 2) are positive indicating that MHAB is more polar than MHA_2 and MHB_2. The positive and negative log K values of equilibria (21) and (22) (Table 2) respectively indicate that MH_2AB is more polar than MHA_2 but less polar than MHB_2. To account for all these observations the following structures (Chart 1) for the protonated chelates are proposed.

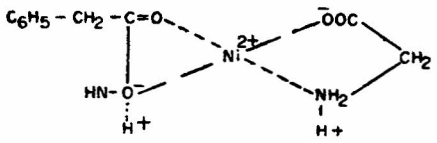
The K^{M}_{MAB} was found to be greater than either $K^{M}_{MA_2}$ or $K^{M}_{MB_2}$ indicating that the formation of ternary chelate is favoured over both the binary chelates. That log K value (1·15) of $MA_2+MB_2 \rightleftharpoons 2$ MAB is significantly greater than the statistically expected[14] value (0·6) also supports the above contention. Hence, it could be inferred that the ternary chelate would not disproportionate into binary chelates but instead would be formed from them. The log K values of a number of equilibria (4, 5, 18, 19, 27, Table 2) showing the formation of protonated ternary



Diprotonated Ni (II) Glycine Complex



Diprotonated Ni (II) PAHA Complex



Diprotonated Ni (II) PAHA-Glycine Complex

CHART 1

chelates indicated that these are favoured over the corresponding binary chelates. These observations also suggest that the ternary chelates are more polar than the binary chelates.

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